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Air Monitoring Directive

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Sour Gas Industry

Alberta
ENVIRONMENT

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SOUR GAS INDUSTRY

AIR MONITORING DIRECTIVE

AMD-80-2

ISSUED: June 1, 1980

R. N. BRIGGS, M.Sc., P.Eng.
DIRECTOR, DIVISION OF POLLUTION CONTROL

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FOREWORD

This Air Monitoring Directive deals with the reporting format and air quality monitoring requirements as they relate specifically to the Sour Gas Industry.

All requirements in this directive come into effect June 1, 1980, unless otherwise stated in an individual section.

This directive supersedes Air Monitoring Directive (AMD) 76-1.

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I. INTRODUCTION

Attached to each Licence-to-Operate under the Clean Air Act are a number of terms, conditions, and requirements; one part of which is concerned with "Monitoring and Returns." This directive, pursuant to Section 12 of the Clean Air (General) Regulations 216/75, is designed to specify acceptable monitoring methods and to standardize the format of the "Returns." Note that only those portions of this directive which pertain to the individual plant Licence-to-Operate need be taken into consideration.

The monitored data must be summarized, tabulated, and forwarded to the Director of Pollution Control of Alberta Environment in the form of a monthly report. In addition, the Director of Pollution Control must receive an annual report, notification of uncontrolled releases, and notification of non-compliance with any licence condition or regulation (herein called a "violation").

This directive deals first with the reporting requirements, and then covers the air monitoring operations. Examples and supplemental information appear in the appendices.

II. SOUR GAS INDUSTRY REPORTING REQUIREMENTS

A. General

1. All ambient air monitoring reports shall be addressed as follows:

   Mr. R. N. Briggs, M.Sc., P.Eng.
   Director, Division of Pollution Control
   Alberta Environment
   6th Floor, Oxbridge Place
   9820 - 106 Street
   Edmonton, Alberta
   T5K 2J6

2. The heading of the covering letter of any report shall make reference to the plant name, plant operator, plant licence number, type of report, and report date.

3. All reports shall be legible and shall contain the pertinent information as specified in this directive.

4. All reports shall be complete. No partial reports will be accepted. The only exception is that noted in the section on "Violation Reports."

B. Monthly Reports

1. All air monitoring data shall be compiled and submitted before the end of the month following that for which the observations were made. If a report is delayed, the reasons for the delay shall be submitted prior to the reporting deadline.

2. The monthly report shall contain completed copies of:

   a. The summary sheet.

   b. The table of total sulphation and hydrogen sulphide data.

   c. The table of half-hour average sulphur dioxide concentrations.

   d. The table of half-hour average hydrogen sulphide concentrations.

   e. The table of one-hour average wind speeds and wind directions.

   f. An annotated photocopy of the recorder charts or digital print-out during calibration.

   g. Calibration graphs.

   h. Continuous stack emission data as specified in Section IV, subsection A.3 of this report.

   The forms to be completed for (a) to (e) and (h) are given in Appendix A along with examples of (f) and (g).

3. The covering letter shall contain:
   a. An explanation of all exposure station results in excess of the Alberta Environment guidelines for total sulphation and hydrogen sulphide.
   b. A discussion of the problems encountered if any monitoring instrument is operational less than 90% of the time.
   c. An explanation for any hydrogen sulphide exposure levels greater than total sulphation levels at the same station.
4. The required air monitoring data must be submitted at all times, unless permission is granted in advance from the Air Quality Control Branch.

C. Annual Report

1. Annual reports shall be submitted no later than February 14 of the year succeeding the report year, unless valid reasons for the delay are forwarded. The report year begins in December of the previous calendar year and ends in November of the report year. The report year consists of four consecutive seasons beginning with winter and ending with fall. The seasonal breakdown is as follows:

   Winter - December, January, February

   Spring - March, April, May

   Summer - June, July, August

   Fall - September, October, November

2. The annual reports shall include:

   a. A summary of any significant environmental studies conducted in the vicinity of the plant such as vegetation or soil studies.

   b. A summary of extensions or alterations of the facility (e.g. sulphur plant tail gas clean-up, sulphur storage and handling changes) that will affect atmospheric emissions including photographs or 35 mm slides.

   c. A review of total sulphation and H_2S exposure cylinder data. The data shall include:

      (i) tables of seasonal and annual averages for each station;

(ii) lines of equal value on a seasonal basis, if more than 16 stations are maintained.

d. For plants required to conduct continuous ambient monitoring for more than six months of the year, an evaluation of the data shall contain:

(i) a listing of the number of minutes of SO_2 and H_2S readings in excess of the Clean Air (Maximum Levels) Regulations for each month for each monitoring unit;

(ii) the major reasons for the excessive readings noted in d. (i), and an explanation of the corrective action taken to reduce future occurrences;

(iii) frequency distribution tables for wind speed and direction; tables shall be drawn up for each season and for each station (refer to Appendix B);

(iv) a percent frequency distribution table of the half-hour average SO_2 concentrations on a seasonal and annual basis for each station, using three concentration ranges: <.10 ppm, .10 ppm to .20 ppm, and >.20 ppm.

e. For plants required to conduct continuous ambient monitoring for six months of the year or less, evaluation of the data shall contain:

(i) a listing of the number of minutes of SO_2 and H_2S readings in excess of the Clean Air (Maximum Levels) Regulations for each month for each monitoring unit;

(ii) the major reasons for the excessive readings noted in e.(i), and an explanation of the corrective action taken to reduce future occurrences;

(iii) frequency distribution tables for wind speed and direction; tables shall be drawn up for each station for the duration of the monitoring period;

(iv) a percent frequency distribution table of the half-hour average SO_2 concentrations on an annual basis for each station, using three concentration ranges: <.10 ppm, .10 ppm to .20 ppm, and >.20 ppm.

D. Violations

1. Ambient

a. The Clean Air (Maximum Levels) Regulations refer to running averages. A "violation" of the Clean Air (Maximum Levels) Regulations occurs when there is an average concentration in excess of the Maximum Permissible Concentration for the specified averaging period.

b. Violations of the Clean Air (Maximum Levels) Regulations shall be reported in terms of the time intervals and total duration (in minutes for half-hour and one-hour averages; in hours for 24-hour averages).

c. Whenever the "instantaneous" SO_2 concentration (recorder trace or one-half minute digital value) exceeds 0.20 ppm, running half-hour averages shall be calculated at five-minute intervals from the time of the first peak in excess of 0.20 ppm until such time as the "instantaneous" concentration remains below 0.20 ppm for at least one-half hour. (See Appendix C for an example of the calculation and reporting of ambient violations.)

d. Whenever the "instantaneous" SO_2 concentration exceeds 0.17 ppm, running one-hour averages shall be calculated at five-minute intervals

from the time of the first peak in excess of 0.17 ppm until such time as the "instantaneous" concentration remains below 0.17 ppm for at least one-half hour.

e. Whenever the half-hour SO_2 concentration exceeds 0.10 ppm, a 24-hour running average shall be calculated using the preceding 47 half-hour readings (i.e. the half-hour average exceeding 0.10 ppm shall be the 48th half-hour in the calculation).

f. Whenever the "instantaneous" H_2S concentration (recorder trace or one-half minute digital value) exceeds 12 ppb, running half-hour averages shall be calculated at five minute intervals from the time of the first peak in excess of 12 ppb until such time as the "instantaneous" concentration remains below 12 ppb for at least one-half hour.

g. Whenever the H_2S concentration exceeds 10 ppb, running one-hour averages shall be calculated at five minute intervals from the time of the first peak in excess of 10 ppb until such time as the "instantaneous" concentration remains below 10 ppb for at least one-half hour.

h. Whenever the half-hour H_2S concentration exceeds 6 ppb, a 24-hour running average shall be

calculated using the preceding 47 half-hour readings (i.e. the half-hour average exceeding 6 ppb shall be the 48th half-hour in the calculation).

i. The reporting of H_2S violations measured by spot tape samplers shall be on the clock half-hours.

j. The calculation method in (c) to (h) shall be as accurate as possible. In the absence of an integrator, planimeter, digitizer, or other electromechanical device, manual digitization and averaging shall be performed. These calculations must be completed soon after the detection of any apparent violation because confirmation of the violation must be forwarded as noted in (l).

k. In areas of environmental concern there may be requirements for continuous integration, telemetry, or other alarm techniques so that the operator can immediately implement remedial action to reduce high concentrations of SO_2 or H_2S.

l. Upon detection of an apparent ambient violation, the Air Quality Control Branch shall be notified by telephone (427-5893 during office hours, or 1-800-222-6514 after hours) during the next 24 hours and the following information supplied:

(i) name of plant;

(ii) identification of monitoring unit, e.g. Trailer No. 1;

(iii) date(s) of apparent violation(s);

(iv) time intervals and durations as per (b);

(v) peak average reading for the duration of the violation;

(vi) general atmospheric conditions including wind speed and direction;

(vii) cause of high readings, and any remedial action taken.

m. Within 72 hours of verbal notification of an apparent violation, the information required in (l) shall be confirmed in writing and forwarded to the Director of Pollution Control. If after verbal notification, there is in fact no violation, written confirmation to that effect shall be submitted.

2. Stack

a. The licences issued under the Clean Air Act contain requirements limiting the emission rate or concentration of air contaminants from individual plant stacks. In addition, these licences may also specify minimum operating conditions (e.g. minimum stack temperature). A "violation" of the licence-to-operate occurs

when any condition within a plant licence has not been met.

b. All time periods for determining licence compliance shall be running averages unless specified otherwise by the Director of Pollution Control.

c. Violations of the licence requirements shall be reported in terms of time intervals and total duration (in minutes for half-hour averages).

d. Violations of stack exit temperatures shall be reported in accordance with the Energy Resources Conservation Board's information letter (IL 79-16).

e. Upon detection of an apparent stack violation, the Air Quality Control Branch shall be notified by telephone (427-5893 during office hours, or 1-800-222-6514 after hours) and the following information supplied:

(i) name of plant;

(ii) date(s) of apparent violation(s);

(iii) identification of stack, licence condition violated, and the extent to which the condition is violated;

(iv) time intervals and durations as per (c);

(v) cause of high readings and any remedial action taken.

f. Within 72 hours of verbal notification of an apparent violation, the information required in (e) shall be confirmed in writing and forwarded to the Director of Pollution Control. If after verbal notification, there is in fact no violation, written confirmation to that effect shall be submitted.

III. SOUR GAS INDUSTRY AIR MONITORING OPERATIONS REQUIREMENTS

A. Site Selection

1. Stations shall be located in accordance with the Standard Site Criteria (Appendix D) wherever and whenever possible.
2. In forested and populated areas it will generally be difficult to find ideal sites for static monitoring stations. Areas that are relatively open, especially in the direction of the plant, shall be selected. The top of a fence post is often a convenient mount. Static monitoring stations should never be located under trees, near hedges, in contact with buildings, or on the side of power/telephone poles.
3. In forested areas a site meeting the exposure criterion for the sampling inlet of a continuous monitor can be found by locating the station in the center of an existing clearing that has a diameter of about four tree-canopy heights (typically 60 to 120 m). The wind instrument must then be installed at a height equal to or greater than four-fifths of the tree-canopy height.
4. A clearing that is only three tree-canopy heights in diameter may be used if the station is located off center such that it is two tree-canopy heights from the trees in the direction of the plant. The wind

instrument must then be installed at a height equal to or greater than nine-tenths of the tree-canopy height.

5. Clearings smaller than three tree-canopy heights in diameter may be used if the sampling inlet is raised to meet the thirty-degree exposure criterion in the direction of the plant and a forty-five-degree exposure in all other directions. Wind instruments must be raised high enough to meet the six-degree exposure criterion.
6. If no clearings are available, the wind instrument shall be erected two metres above the forest canopy and the sampling inlet shall be placed at least one-half metre above the tree-canopy.
7. Sampling lines cannot be much longer than about nine metres without encountering condensation problems. If longer lines are to be used, insulation, heating tapes, or other measures to prevent condensation are required.
8. Before any new continuous monitoring station is installed, the Air Quality Control Branch shall be contacted to arrange for an inspection of the site.
9. All sampling lines shall be made of teflon, glass, or other inert material approved by the Air Quality Control Branch. (N.B. - recent studies have shown

that stainless steel sampling lines absorb H_2S and SO_2).

10. The end of a sampling line may be used as a sampling inlet only if shaped into an inverted U.

11. All existing stations will be inspected by Alberta Environment. Where sites do not conform to the specifications of this section, relocation or other action may be required.

B. Network and Site Documentation

1. The documentation described in Appendix E with qualifications noted in (2) to (6) below governs new air monitoring networks. Prior to the installation of the stations, this documentation shall be forwarded to the Air Quality Control Branch for approval.
2. Documentation for stations that have already been approved by the Air Quality Control Branch shall be submitted only when a change takes place.
3. The area and topographic maps shall also indicate the location of the plant, all wells, and all battery sites.
4. In addition to the full size maps, reductions to 8 1/2" x 11" shall be included if the reduced maps are legible.
5. An aerial photograph of each continuous monitoring station shall be submitted if it is readily available.
6. Only one cross-section sketch is required. This sketch is to show obstacles for 500 m on either side of the continuous monitoring station along the line drawn from the plant through the monitoring station. The vertical scale may be exaggerated to show detail and elevation angles to the tops of the obstacles.

C. Continuous Ambient Air Monitoring Operations

1. General

a. The number of continuous monitoring stations for the determination of sulphur dioxide and hydrogen sulphide in ambient air that a sour gas processing plant is required to have is determined by the following schedule:

Maximum Allowable SO_2 emission rate (tonnes/day)	No. of Continuous Monitoring Stations	Mo./Yr.
≥244	5	12
≥183, <244	4	12
≥122, <183	3	12
≥61, <122	2	12
≥30, <61	1	12
≥20, <30	1	9
≥10, <20	1	6
≥6, <10	1	3
≥2, <6	1	2
<2	As required	As required

b. Each instrument shall be operational a minimum of 90% of the time. The percentage of time that each instrument was operating shall be given on the summary form of the monthly report. The time periods utilized for calibrations--internal

source and external multi-point--are not considered down-time.

c. Where continuous monitoring is conducted 12 months of the year, failure to meet the above requirement may result in a requirement for backup equipment.

d. Where continuous monitoring is conducted less than 12 months of the year, failure to meet the 90% minimum operational time automatically results in a requirement for the survey to be extended until the number of days in excess of the 10% down-time have been made up. For example, if a monitor is inoperative for five days during a 30 day survey, the survey shall be extended for two days.

e. Whenever the 90% requirement is not met, complete details of the problems encountered shall be included in the covering letter of the monthly report.

f. Where continuous monitoring is conducted for less than 12 months of the year, one survey shall be conducted during the annual plant turnaround and include the period one week prior to and one week after the turnaround.

g. Where plants are conducting air monitoring surveys for less than 12 months per year, the

Air Quality Control Branch shall be notified of the intent to set up the monitoring trailer at least one month before the survey commences. If the survey report period differs substantially from the proposed monitoring period, an explanation shall be forwarded with the survey report.

h. All recorder charts or digital print-outs shall be retained for a period of 24 months and shall be made available to the Air Quality Control Branch upon request.

i. The time periods used in the monthly report tables shall correspond to clock intervals and shall be kept in Mountain Standard Time throughout the year.

j. Continuous ambient air monitoring stations without telemetry shall be checked at least once per day, or at some other frequency approved by the Air Quality Control Branch.

k. All data shall be reported in the format shown in Appendix A.

l. The choice of any instrument to be used in a continuous air monitoring station shall be reviewed by the Air Quality Control Branch prior to installation.

2. Sulphur Dioxide

a. In digital systems "continuous" shall mean that concentration values are obtained at least twice every minute.

b. All concentration values shall be rounded off to the nearest 0.01 ppm.

c. All SO_2 instruments equipped with filters in the sampling head must be equipped with heaters.

d. Zero checks and one-point span gas checks shall be conducted on the SO_2 instruments at least once per week.

e. The SO_2 instruments must be calibrated by means of permeation tubes at three or more concentrations (excluding zero) a minimum of once per month. Where a calibration results in a zero and/or span adjustment in excess of 10% being made, the instrument must be recalibrated.

f. During calibration of SO_2 instruments, it is recommended that the selection of calibration points be such that points are included both below and above the pertinent ambient standards (i.e. SO_2 half-hour maximum ground level concentration = 0.20 ppm). In addition, it is recommended that the calibration points fall within a range of 15 to 65% of full scale range on the monitoring instrument recorder output.

g. During calibrations of SO_2 instruments, sufficient time shall be allotted for stabilization of the recorder output after SO_2 adjustments have been made. It is recommended that the SO_2 input level be maintained for a minimum of 20 minutes after the instrument has fully stabilized at that level. Inability to maintain a constant trace at a specific SO_2 input level could indicate problems with the calibration rig or the monitoring instrument.

h. Noise levels should not exceed 2% of recorded value during calibration of SO_2 instruments.

i. When the calibration obtained is unsatisfactory, the calibration procedure shall be repeated until a satisfactory calibration has been obtained.

j. Internal source calibrations are optional. In cases where this calibration method is not being used, the internal permeation source must be properly sealed.

k. Calibration checks will be carried out by Alberta Environment on SO_2 instruments selected at random. If these checks prove that a particular instrument is unacceptable, modification or replacement of the unit will be required.

l. A legible photocopy of the recorder chart or digital print-out during calibration, together with interpretive notes shall be submitted as part of the monthly report. This photocopy or digital print-out shall illustrate:

(i) the internal source calibration;

(ii) the start and finish times;

(iii) the baselines before and after calibration;

(iv) stabilization at each concentration;

(v) The SO_2 concentration at each calibration point;

(vi) a recorder range of approximately 1 ppm full scale.

m. A calibration graph with a straight line passing through the three calibration points and zero shall also be submitted as part of the monthly report. When the straight line does not pass through zero and the three calibration points, action should be taken to determine the cause of the deviations.

3. Hydrogen Sulphide

a. Instrument systems other than spot tape samplers:

(i) In digital systems "continuous" shall mean that concentration values are obtained at least twice every minute.

(ii) All concentration values shall be rounded off to the nearest 1 ppb.

(iii) The H_2S instruments shall be calibrated by means of permeation tubes, wafers, or equivalent at three or more concentrations (excluding zero) once a month. Where a calibration results in a zero and/or span adjustment in excess of 10% being made, the instrument must be recalibrated.

(iv) During calibration of H_2S instruments it is recommended that the selection of calibration points be such that points are included both below and above the pertinent ambient standards (i.e. H_2S half-hour maximum ground level concentration = 12.0 ppb). In addition, it is recommended that the calibration point fall within a range of 15 to 65% of full scale range on the monitoring instrument recorder output.

(v) During calibration of H_2S instruments, sufficient time shall be allotted for

stabilization of the recorder output after H_2S input adjustments have been made. It is recommended that the H_2S input level be maintained for a minimum of 20 minutes after the instrument has fully stabilized at that level. Inability to maintain a constant trace at a specific H_2S input level could indicate problems with the calibration rig or the monitoring instrument.

(vi) Noise levels should not exceed 2% of recorded value during calibration of H_2S instruments.

(vii) Calibration checks will be carried out by Alberta Environment on H_2S instruments selected at random. If these checks prove that a particular instrument is unacceptable, modification or replacement of the unit will be required.

(viii) A legible photocopy of the recorder chart during calibration, together with interpretive notes shall be submitted as part of the monthly report. This photocopy shall illustrate:

- the instrument calibration;

- the baselines before and after calibration;
- stabilization at each concentration;
- the H_2S concentration at each calibration point;
- a recorder range of approximately 60 ppb full scale.

(ix) A calibration graph with a straight line passing through the three calibration points and zero shall also be submitted as part of the monthly report. When the straight line does not pass through zero and the three calibration points, action should be taken to determine the cause of the deviations.

b. Spot tape monitoring instrument systems:

(i) The spot tape monitoring instrument shall be set to give half-hour spots.

(ii) Spot tapes must not be reused under any circumstances.

(iii) All concentrations shall be reported in parts per billion (ppb).

(iv) Spot tapes should be read within 24 hours of sampling.

c. A comparative study of hydrogen sulphide monitors by Alberta Environment has indicated

that spot tape samplers may not provide as adequate sensitivity as a continuous type hydrogen sulphide analyzer. In view of this, all hydrogen sulphide monitoring shall be changed to continuous monitoring methods by January 1, 1982. (Guidelines for selecting H_2S monitoring instrumentation are available from the Air Quality Control Branch.)

4. Wind

   a. Wind vanes shall be oriented such that a north wind is indicated for wind blowing from the true north.

   b. Wind directions shall be reported using eight compass points (N, NE, E, SE, S, SW, W, NW).

   c. Wind speeds shall be reported to the nearest kilometre per hour (km/h).

   d. All wind instruments shall have a starting threshold no greater than 1.0 km/h.

   e. A wind shall be reported as "calm" only if the hourly average speed is 1.0 km/h or less.

   f. Wind instruments shall be maintained in good running condition. Damaged cups and vanes shall be replaced immediately. Bearings shall be checked at least annually; however, should significant friction develop, they should be checked immediately and replaced.

D. Static Monitor Operations

1. General

a. The number of static monitoring stations that a sour gas processing plant is required to have is determined by the following schedule.

Maximum Allowable SO_2 emission rate (tonnes/day)	No. of Static Monitoring Stations
≥244	40
≥183, <244	35
≥122, <183	30
≥61, <122	25
≥30, <61	20
≥20, <30	16
≥10, <20	12
≥6, <10	8
≥2, <6	4
<2	2

b. Care shall be exercised at all times in the preparation, handling, and analysis of exposure stations.

c. Operation of exposure stations shall not be interrupted without the authorization of the Air Quality Control Branch.

d. Exposures shall coincide as closely as possible with each calendar month.

e. All data shall be reported in the tables shown in Appendix A. Note that the laboratory responsible for the analysis must be identified and that the results must be certified with the signature of an authorized staff member of the laboratory.

2. Total Sulphation and Hydrogen Sulphide Exposure Stations

a. If any hydrogen sulphide level is in excess of 0.10 SO_3 equivalent mg/day/100 cm^2 or if any total sulphation level is in excess of 0.50 SO_3 equivalent mg/day/100 cm^2, an explanation of the high levels shall be included in the covering letter of the monthly report.

b. Subsection (a) notwithstanding, if any exposure station shows a substantial increase over usual levels, an explanation shall be included in the covering letter of the monthly report.

c. If the hydrogen sulphide level exceeds the total sulphation level at the same station, this shall be noted in the covering letter of the monthly report and an explanation of the discrepancy included.

d. Existing networks may change over to total sulphation plates from the glass jar cylinders, provided that both systems are maintained for a minimum of three months at each station and the results are comparable. New networks may use total sulphation plates from the outset.

e. The accepted procedure for determination of total sulphation in ambient air is given in Appendix F.

f. Only the zinc acetate method for the detection of H_2S is acceptable at this time. The accepted procedure for determination of hydrogen sulphide in ambient air is given in Appendix G.

g. Any variation in exposure cylinder techniques such as "H_2S exposure strips" must be approved by Alberta Environment prior to use.

h. All laboratories performing exposure station analysis shall participate in the Air Quality Control Branch Assurance Program. Laboratories that have not participated in the assurance program shall contact the Air Quality Control Branch prior to performing any analyses for reports.

E. Soil pH Monitoring

1. General

a. Effective January 1, 1980, sulphur dustfall monitoring shall be replaced by soil pH testing (refer to the Energy Resources Conservation Board information letter IL 79-22).

b. Soil pH testing shall be carried out once per year between mid-September and freeze up. An attempt should be made to do the annual sampling at the same time each year at a specific location.

c. It is recommended that a titration curve for determination of the buffering capacity of the soil be submitted for the first two years of soil pH monitoring.

d. The results of the analysis shall be reported to Alberta Environment within 60 days from the date of sampling.

2. Sampling

a. Sampling should be done in the predominant downwind direction with one sample point in the direction of least wind.

b. Distances - Predominant downwind: 50 and 500 metres; one, two, and eight kilometres. Least wind: four kilometres.

c. It would be preferable to have each sampling distance paired approximately 50 to 100 metres apart. Wet, seep, and disturbed areas should be avoided in selecting a sampling site.

d. Depth - 0 to 5 centimetres and 5 to 15 centimetres.

e. Sampling procedure - 15 to 20 cores taken randomly within a five metre radius of each sampling site to produce a composite sample for each site.

3. Analysis

Analysis of the composite samples for each sample point is described in detail in Appendix H.

IV. SOUR GAS INDUSTRY SOURCE EMISSION REPORTING REQUIREMENTS

A. Monthly Reports

1. All stack survey results and continuous stack emission monitoring results compiled during the month shall be sent to the Energy Resources Conservation Board.
2. The format to be used for reporting source emission results will be specified by the Energy Resources Conservation Board.
3. The only information required to be submitted to Alberta Environment in the monthly reports includes:
   a. Stack emissions in tonnes SO_2 (total for the month.
   b. Number of days with stack violations during the month.
   c. The concentration of sulphur dioxide in the gases being exhausted to the atmosphere from the incinerator stack in ppm.
   d. The rate of release of sulphur dioxide to the atmosphere from the incinerator stack in tonnes.
   e. The daily minimum incinerator stack temperature in degrees centigrade (°C).
   f. The rate of release of sulphur dioxide to the atmosphere from the flare stack in tonnes.

   The information in (a) and (b) is to be recorded on the ambient air "Monthly Report Summary" sheet; the

information in (c) to (f) is to be recorded on the "Continuous Stack Emission Monitoring Results" sheet (Appendix A).

B. Annual Report

1. The annual report on source emissions will be sent to the Energy Resources Conservation Board.
2. The format of the report will be specified by the Energy Resources Conservation Board.

C. Violations

1. Source emission violations are to be reported to Alberta Environment.
2. The only information required by Alberta Environment on monthly reports is the number of days during the month on which stack violations occurred. This information is to be recorded on the "Monthly Report Summary" sheet.

V. SOUR GAS INDUSTRY SOURCE EMISSION MONITORING OPERATIONS REQUIREMENTS

A. Stack Emission Surveys

The procedure to be followed for stack emission surveys is outlined in the Alberta Stack Sampling Code, Publication No. SSC-1/76.

B. Continuous Stack Emission Monitoring Operations

1. All sour gas processing plants producing more than 50 long tons of sulphur per day or emitting more than 5 long tons per day shall continuously monitor stack gases for sulphur dioxide concentration, volume flowrate, temperature, and oxygen content.
2. Operation requirements for continuous stack emission monitoring of sulphur dioxide total flue gas flow rate, and stack flue gas exit temperature will be specified by the Energy Resources Conservation Board.

APPENDIX A

SAMPLE FORMAT OF THE MONTHLY REPORT

MONTHLY REPORT SUMMARY

PLANT OPERATOR

PLANT LOCATION

LICENCE NUMBER | MO. | YR.

AL

00

INCINERATOR STACK EMISSIONS IN TONNES SO_2 (TOTAL FOR MONTH)

FLARE EMISSIONS IN TONNES SO_2 (TOTAL FOR MONTH)

NO. OF DAYS WITH STACK VIOLATIONS (TOTAL FOR MONTH)

NO. OF STATIC MONITORING STATIONS EXCEEDING GUIDELINES

TOTAL SULPHATION | H_2S

AMBIENT VIOLATIONS

00=NO 01=YES

SO_2 | H_2S

STN. NO.

% OF TIME INSTRUMENTS OPERATIONAL

SO_2 | WIND | H_2S

MAX. 1/2 HR SO_2 CONC. (PPM)

NO. OF 1/2 HR SO_2 READINGS >0.10 PPM

MAX. 1/2 HR H_2S CONC. (PPB)

SIGNATURE OF COMPANY REPRESENTATIVE

FOR ALBERTA ENVIRONMENT USE ONLY

88

97

98

99

SAMPLE OF

MONTHLY REPORT SUMMARY

F & G OIL & GAS LTD.
PLANT OPERATOR

Fox Creek
PLANT LOCATION

LICENCE NUMBER	MO.	YR.
80 AL 000	01	80

INCINERATOR STACK EMISSIONS IN TONNES *SO_2 (TOTAL FOR MONTH)	FLARE EMISSIONS IN TONNES *SO_2 (TOTAL FOR MONTH)	NO. OF DAYS WITH STACK VIOLATIONS (TOTAL FOR MONTH)
832.8	45.8	06

NO. OF STATIC MONITORING STATIONS EXCEEDING GUIDELINES	
TOTAL SULPHATION	H_2S
01	00

AMBIENT VIOLATIONS 00=NO 01=YES	
SO_2	H_2S
00	01

STN. NO.	% OF TIME INSTRUMENTS OPERATIONAL			MAX. 1/2 HR SO_2 CONC. (PPM)	NO. OF 1/2 HR SO_2 READINGS >0.10 PPM	MAX. 1/2 HR H_2S CONC. (PPB)
	SO_2	WIND	H_2S			
1	99.9	53.5	100.0	0.09	0	11
2	99.2	85.4	100.0	0.04	0	102
3	100.0	95.9	98.9	0.04	0	98

* N.B. - SO_2, not sulphur (S°)

John Doe
SIGNATURE OF COMPANY REPRESENTATIVE

FOR ALBERTA ENVIRONMENT USE ONLY

88

97

98

99

ANNOTATION FOR THE "MONTHLY REPORT SUMMARY" PAGE

1. Licence number refers to the number of the current Clean Air licence issued by Alberta Environment.

2. Month and year refer to the month and year of the report being submitted.

3. The number of days with stack violations refer to the total number of days that:

   a. the concentration of sulphur dioxide in the gases being exhausted to the atmosphere from the sulphur plant incinerator stack exceeds the minimum permissible level;

   b. the rate of release of SO_2 to the atmosphere from the sulphur plant incinerator stack exceeds the maximum permissible level; and

   c. The flue gas emission temperature drops below the minimum permissible temperature.

   If (a), (b), and (c) occur on the same day, only one day of stack violation shall be recorded.

4. The purpose of the "box" on ambient violations is to identify if any violations were recorded. The coding of 00 indicates no violations; the coding of 01 indicates that violations were recorded.

5. Plants that vent SO_2 through points other than an incinerator stack or a flare stack should list their SO_2 emissions under the heading "Process Fuel Emissions" on the "Monthly Report Summary" sheet. The caption "Process Fuel Emissions" should replace the caption "Incinerator Stack Emissions."

Plant Operator _____ Plant Location _____ Monitoring Station _____

Report Month _____

HALF-HOURLY AVERAGE SO_2 CONCENTRATIONS (PPM)

(Page 1)

DATE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	DAILY AVERAGE
1	.xx																								
2	.yy																								
3																									
4																									
5																									
6																									
7																									
8																									
9																									
10																									
11																									
12																									
13																									
14																									
15																									
16																									
17																									
18																									

(format example)

.xx designates the half-hour from 00:00 - 00:30
.yy designates the half-hour from 00:30 - 01:00

Plant Operator | Plant Location | Monitoring Station

Report Month

HALF-HOURLY AVERAGE SO_2 CONCENTRATIONS (PPM)

DATE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	DAILY AVERAGE
19																									
20																									
21																									
22																									
23																									
24																									
25																									
26																									
27																									
28																									
29																									
30																									
31																									
MEAN CONC.																									

Max. Half-hourly avg._____ppm Day _____Time _____
Max. Hourly Average _____ppm Day_____Time _____
Max. Daily Average _____ppm Day_____

Average Concentration for the Period _____ppm

*** Indicates no data due to instrument problems
C - Designates calibration periods

Plant Operator _____ Plant Location _____ Monitoring Station _____

Report Month _____

HALF-HOURLY AVERAGE H_2S CONCENTRATIONS (PPB)

Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	DAILY AVERAGE
1																									
2																									
3																									
4																									
5																									
6																									
7																									
8																									
9																									
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12																									
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15																									
16																									
17																									
18																									

Plant Operator _____ Plant Location _____ Monitoring Station _____

Report Month _____

HALF-HOURLY AVERAGE H_2S CONCENTRATIONS (PPB)

(Page 2)

DATE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	DAILY AVERAGE
19																									
20																									
21																									
22																									
23																									
24																									
25																									
26																									
27																									
28																									
29																									
30																									
31																									
MEAN CONC.																									

Max. Half-hourly Avg. _____ ppb Day _____ Time _____
Max. Hourly Average _____ ppb Day _____ Time _____
Max. Daily Average _____ ppb Day _____

Average Concentration for the period _____ppb

*** Indicates no data due to instrument problems
C - Designates calibration periods.

Plant Operator _____ Plant Location _____ Monitoring Station _____

Report Month _____

DATE	WIND DIRECTION (to 8 compass points) and WIND SPEED (in km/h)																						AVERAGE SPEED
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	
1																									
2																									
3																									
4																									
5																									
6																									
7																									
8																									
9																									
10																									
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27																									
28																									
29																									
30																									
31																									
MEAN SPEED																									

** Indicates no data due to instrument problems

STATIC MONITORING RESULTS

PLANT OPERATOR _____ PLANT LOCATION _____

MONTH _____

Station Number	Total Sulphation	Hydrogen Sulphide	Station Number	Total Sulphation	Hydrogen Sulphide
	SO_3 eq. mg/day/ 100 cm^2			SO_3 eq. mg/day/ 100 cm^2	
1			21		
2			22		
3			23		
4			24		
5			25		
6			26		
7			27		
8			28		
9			29		
10			30		
11			31		
12			32		
13			33		
14			34		
15			35		
16			36		
17			37		
18			38		
19			39		
20			40		

_____
Laboratory Responsible

_____
Signature of Supervisor

CONTINUOUS STACK EMISSION MONITORING RESULTS

PLANT OPERATOR _____ PLANT LOCATION _____

MONTH _____

Date	Sulphur Dioxide in the Incinerator Flue Gas (ppm)	Sulphur Dioxide (mass emission rate as tonnes) from the Incinerator Stack		Incinerator Stack Temperature (°C)	Sulphur Dioxide (mass emission rate as tonnes) from the Flare Stack
	Maximum 1/2-hour reading	Daily Total	Maximum 1/2-hour	Daily Minimum	Daily Total
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
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23					
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25					
26					
27					
28					
29					
30					
31					

SO_2/H_2S CALIBRATION

Plant Operator: _____ Plant Location: _____

Monitoring Station: _____ Date: _____

Make and Model
of Instrument: _____ AMU#: _____ Ser.#: ____

Calibration:
Routine: _____ CM: _____

Audit: _____ Other: _____

Calibration Method: _____ B.P.: _____

Calibration Equipment: _____ Temp.: _____

Permeation Tube #: _____ Permeation Tube Rate: _____

Instrument Settings Before Calibration: After Calibration:

Zero pot: _____ Zero pot: _____

Span pot: _____ Span pot: _____

Inlet flow: _____ Other:

Monitoring Range: _____

Calibration System Flowrate sccm	Calculated Conc. ppm	Indicated Conc. Chart Div./mv	Correction Factor

Average Correction Factor _____

SAMPLE

ALBERTA ENVIRONMENT

SO_2/H_2S CALIBRATION

Plant Operator: _____ Plant Location: _____

Monitoring Station: Shop Date: July 20, 1978

Make and Model of Instrument: Philips AMU#: 397,398 Ser.#: D 991

Calibration:
Routine: SO_2 CM: _____

Audit: _____ Other: _____

Calibration Method: Permeation Tube B.P.: 27.70

Calibration Equipment: Bendix 8861 Temp.: 22°C

Permeation Tube #: 14-4300 Certified at 30°C Permeation Tube Rate: 1520 ng/min

Instrument Settings Before Calibration: After Calibration:

Zero pot: - Zero pot: -

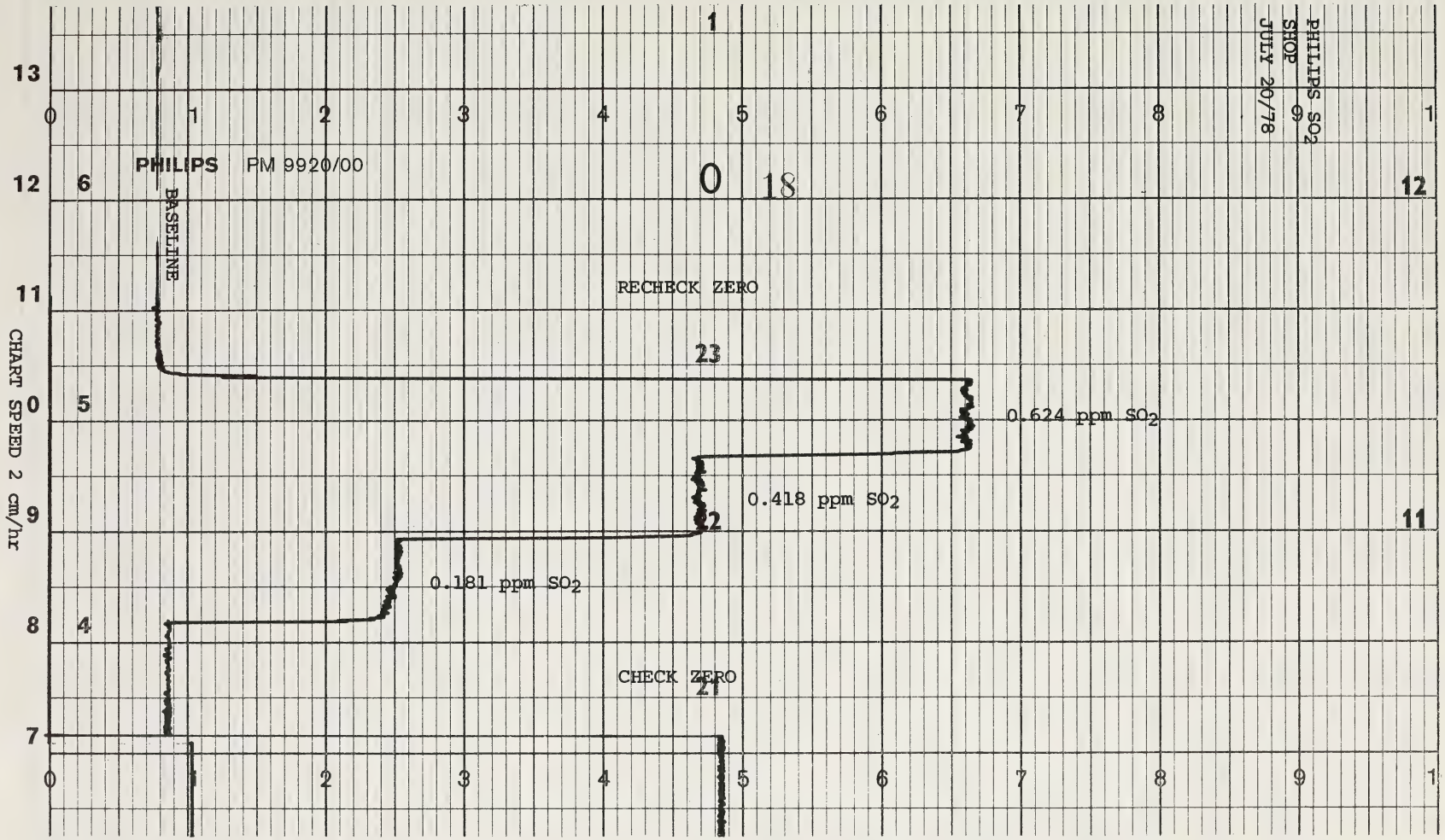
Span pot: - Span pot: -

Inlet flow: Analyzer 275 cc/min; Cell 140 cc/min Other:

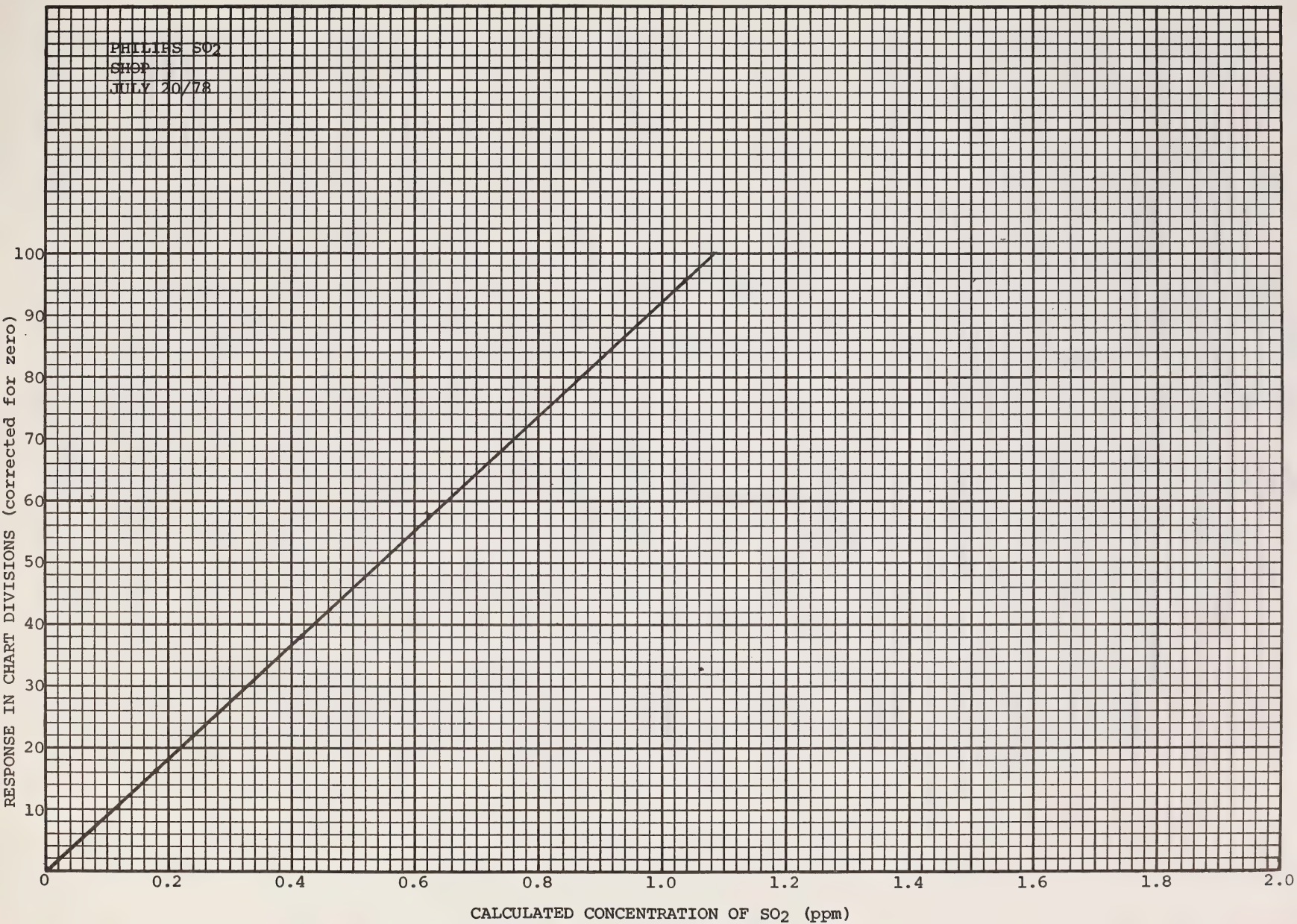
Monitoring Range: 0 - 1.0 ppm

Calibration System Flowrate sccm	Calculated Conc. ppm	Indicated Conc. Chart Div./mv	Correction Factor
Zero Air	0	Chemical zero 8.5 div	-
3206	0.181 ppm	0.167 ppm	1.084
1390	0.418 ppm	0.385 ppm	1.086
930	0.624 ppm	0.577 ppm	1.081

Average Correction Factor 1.084


PHILIPS SO2
SHOP
JULY 20/78
PHILIPS PM 9920/00
0 18
BASELINE
RECHECK ZERO
0.624 ppm SO2
0.418 ppm SO2
0.181 ppm SO2
CHECK ZERO
CHART SPEED 2 cm/hr

7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.



SAMPLE

ALBERTA ENVIRONMENT

SO_2/H_2S CALIBRATION

Plant Operator: _____ Plant Location: _____

Monitoring Station: Redwater - GS043 Date: October 3, 1978

Make and Model of Instrument: Philips AMU#: 305,306 Ser.#: 1372 C

Calibration:
Routine: H_2S CM: _____

Audit: _____ Other: _____

Calibration Method: Permeation Tube B.P.: 27.54

Calibration Equipment: Bendix 8861 Temp.: 24°C

Permeation Tube #: 17-6363 Certified 30°C Permeation Tube Rate: 780 ng/min

Instrument Settings Before Calibration: After Calibration:

Zero pot: - Zero pot: -

Span pot: - Span pot: -

Inlet flow: Analyzer 280 cc/min; Cell 145 cc/min Other:

Monitoring Range: 0 - 1.0 ppm

Calibration System Flowrate sccm	Calculated Conc. ppm	Indicated Conc. Chart Div./mv	Correction Factor
Zero Air	0	Chemical zero 3.6 div	-
6217	0.090 ppm	0.108 ppm	0.833
3475	0.161 ppm	0.193 ppm	0.834
2130	0.263 ppm	0.317 ppm	0.830
1410	0.398 ppm	0.478 ppm	0.833

Average Correction Factor 0.833

PHILIPS H_2S
GS043 - REDWATER
OCTOBER 3/78

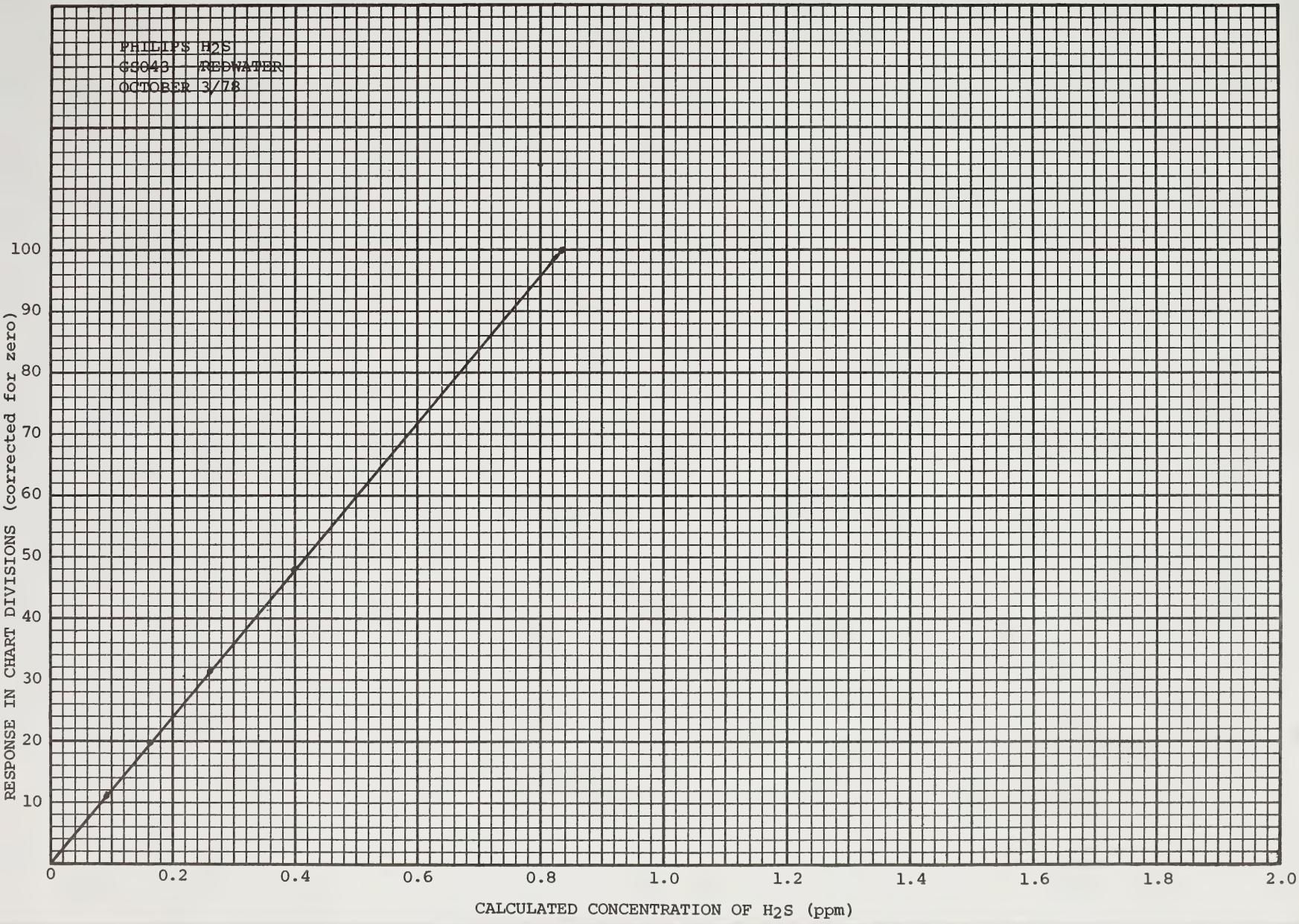
BASELINE
RECHECK ZERO
0.398 ppm H_2S
0.263 ppm H_2S
0.161 ppm H_2S
0.090 ppm H_2S
CHECK ZERO
INTERNAL SOURCE
BASELINE

1500 1400 1300 1200 1100 1000 0900 0800

No. 490489

CHART SPEED 2 cm/hr

KEUFFEL & ESSER CO.



APPENDIX B

SAMPLE OF A FREQUENCY DISTRIBUTION CHART FOR WIND SPEED AND DIRECTION

PERCENTAGE FREQUENCY DISTRIBUTION

PLANT NAME / PLANT LOCATION

SEASON / YEAR

	WIND SPEED (km/h)					
DIRECTION	1 - 5	6 - 11	12 - 19	20 - 28	29 - 38	39 +
N	0.96	2.51	1.93	1.35	0.63	0.16
NE	0.62	1.38	0.62	0.18	0.02	0.00
E	0.81	2.17	1.83	1.27	0.28	0.09
SE	1.21	5.33	7.93	5.67	1.14	0.09
S	1.98	6.86	6.27	1.65	0.19	0.03
SW	1.61	5.58	2.97	0.34	0.01	0.00
W	1.36	4.03	5.17	3.10	0.78	0.41
NW	1.04	2.57	2.81	2.68	1.76	0.82

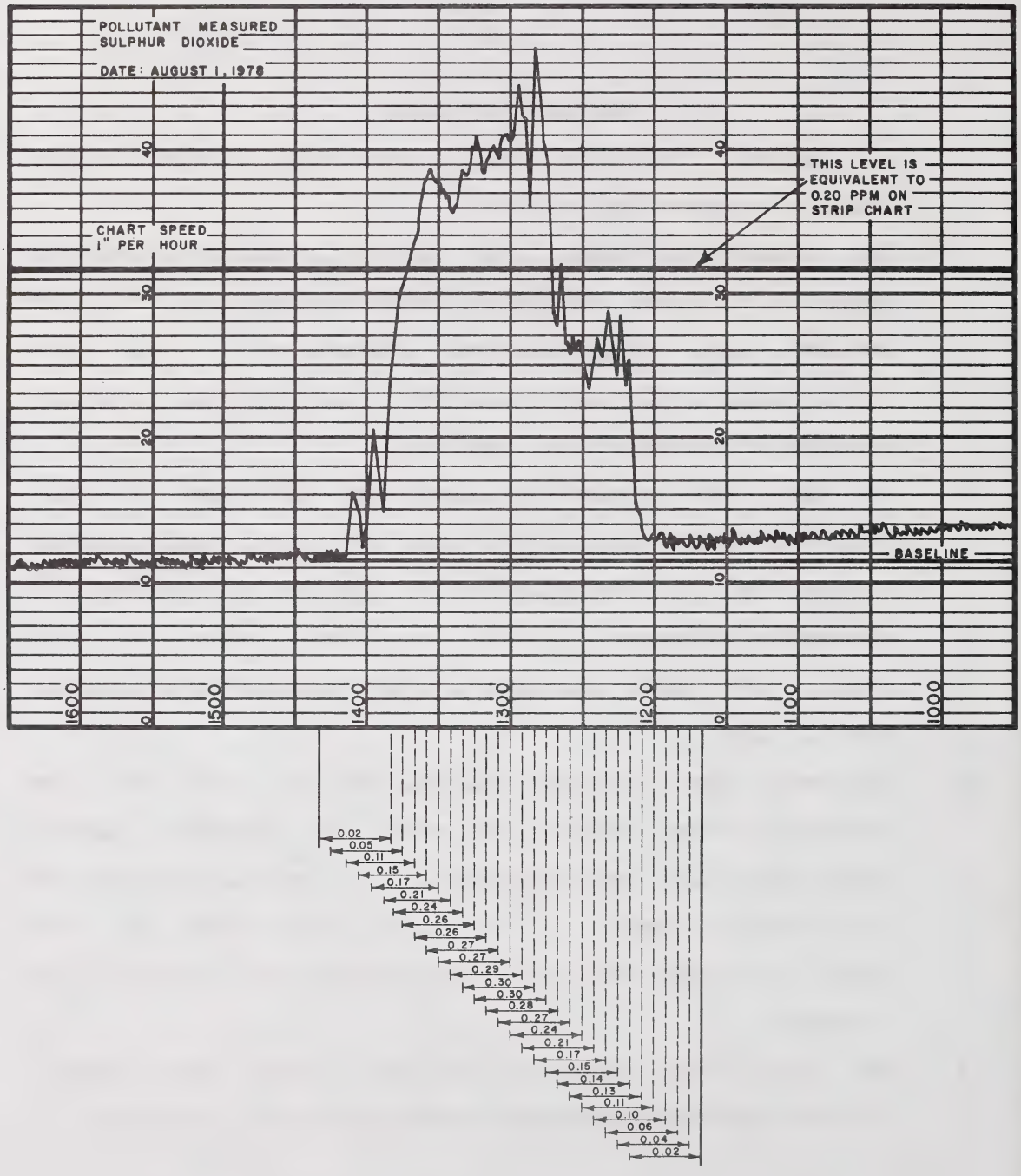
C 7.65%

APPENDIX C

SAMPLE CALCULATION FOR AMBIENT VIOLATIONS

EXPLANATORY NOTES

1. All ambient violations shall be calculated as shown by the examples on pages C-3 and C-4.
2. The examples on pages C-3 and C-4 illustrate integrated traces of half-hour average SO_2 concentrations and one-hour average SO_2 concentrations respectively. All the calculations are running half-hour and one-hour averages based on five minute time intervals.
3. To report the violation illustrated on page C-3, the following format should be used: the half-hour maximum permissible SO_2 concentration of 0.20 ppm was exceeded for 65 minutes on August 1, 1978 from 12:50 hours to 13:55 hours. The peak half-hour average reading for the period was 0.30 ppm.
4. To report the violation illustrated on page C-4, the following format should be used: the one-hour maximum permissible SO_2 concentration of 0.17 ppm was exceeded for 75 minutes on August 1, 1978 from 12:55 hours to 14:10 hours; the peak one-hour average reading for the period was 0.28 ppm.
5. The calculation method and reporting format can be applied to other monitored pollutants such as hydrogen sulphide.

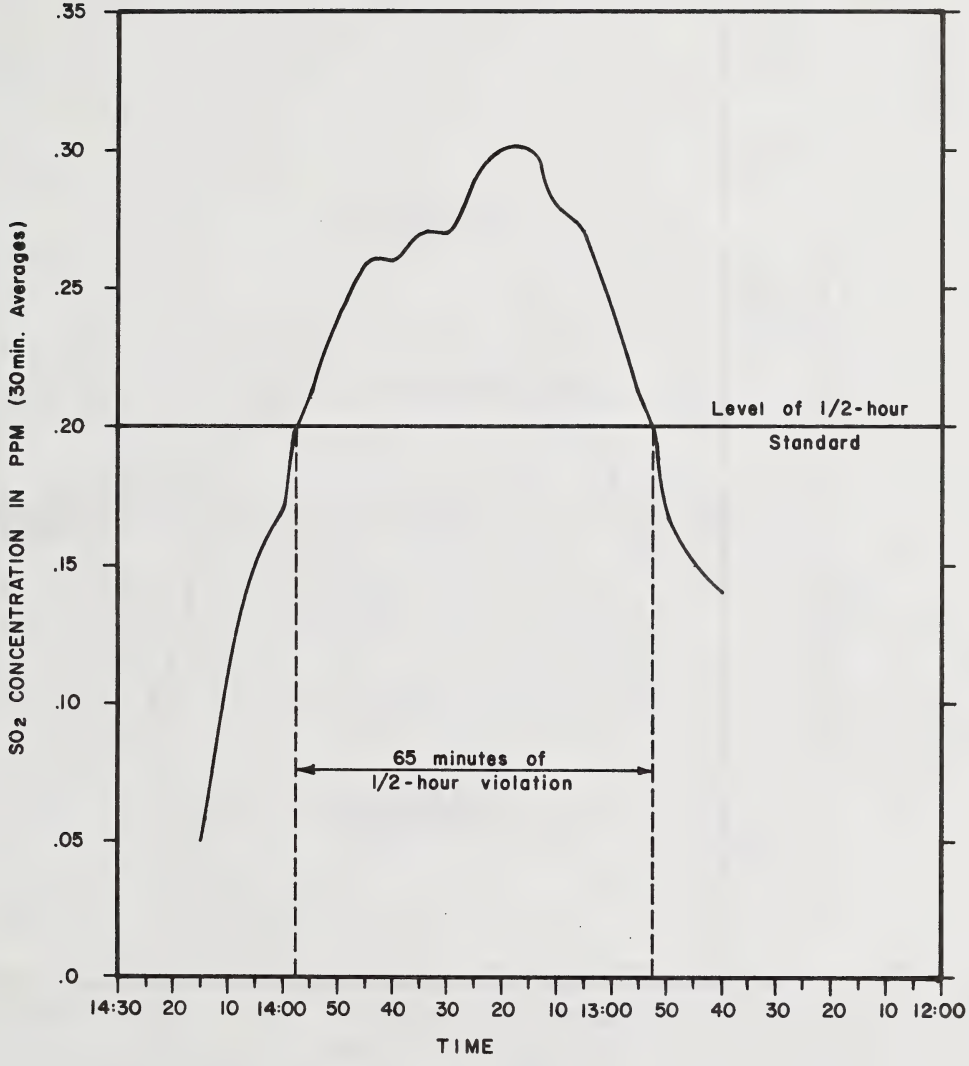


ACTUAL SO_2 TRACE

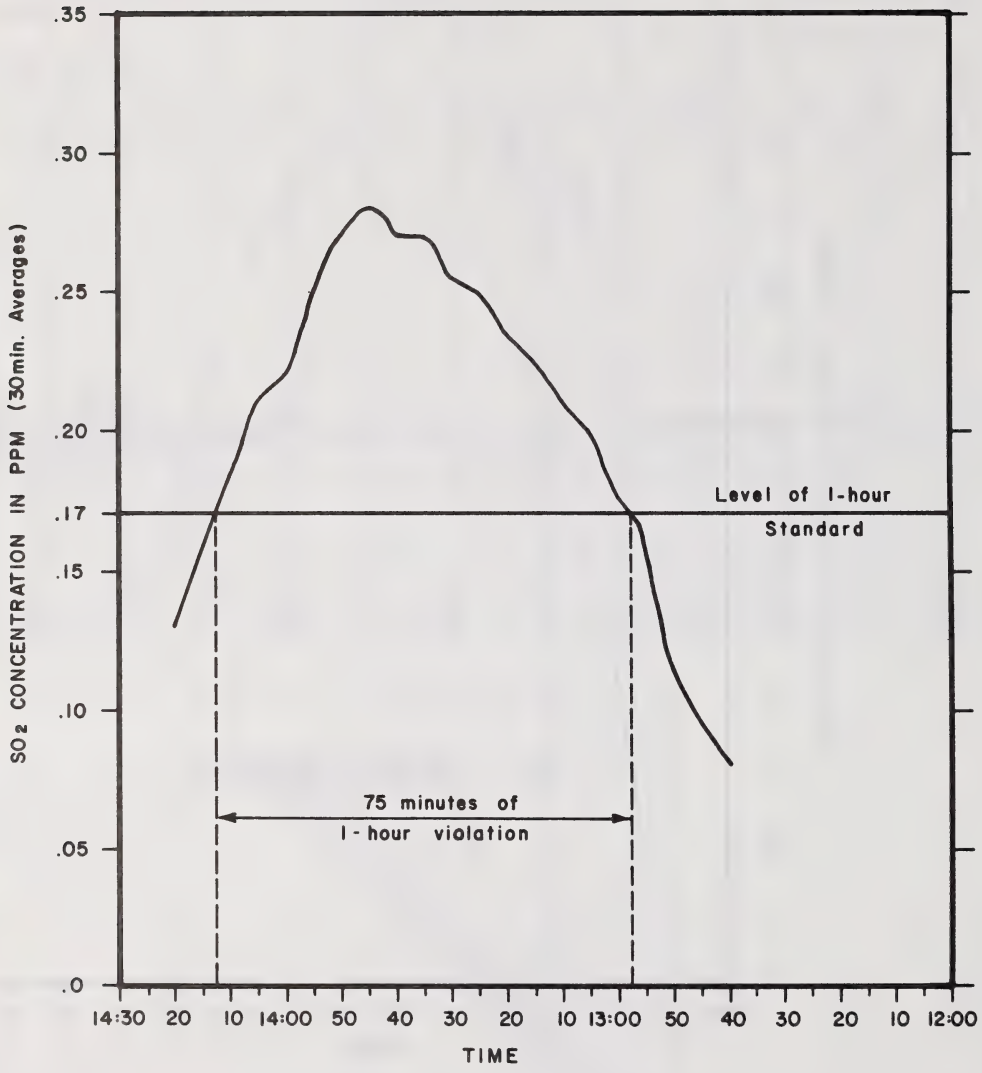
KEY :

⟷ AVERAGE SO_2 CONCENTRATION FOR A 1/2 - HOUR PERIOD E.G. 12:00 - 12:30 : AVERAGE 1/2 - HOUR SO_2 CONCENTRATION IS 0.11 P.P.M.

|| DENOTES A FIVE-MINUTE TIME PERIOD



INTEGRATED TRACE OF 30 MINUTE AVERAGE
SO_2 CONCENTRATIONS CALCULATED AT FIVE MIN. INTERVALS



INTEGRATED TRACE OF 60 MINUTE AVERAGE
SO_2 CONCENTRATIONS CALCULATED AT FIVE MIN. INTERVALS

APPENDIX D

CRITERIA FOR SELECTION OF A STANDARD MONITORING SITE

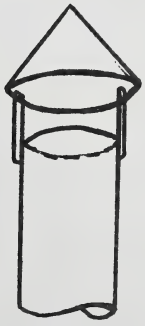
STANDARD SITE CRITERIA

An air monitoring station shall meet the criteria given in the following table:

Site Characteristic \ Station Component	Continuous Monitor Sampling Inlet	Wind Instrument	Static Monitors
Height above ground (m)	Shelter height + at least 0.5 m (3 m min.)	>2.5 times Shelter height (10 m min.)	1 - 3
Elevation angle to top of any obstruction* (degrees)	< 30	< 6	< 30

The diagram on the following page illustrates these criteria.

Sampling inlets are vertical with a protective cover that does not interfere with the free flow of ambient air into the sampling lines. All sampling lines are made of teflon, glass, stainless steel, or other inert material. A design for a sampling inlet is shown below.

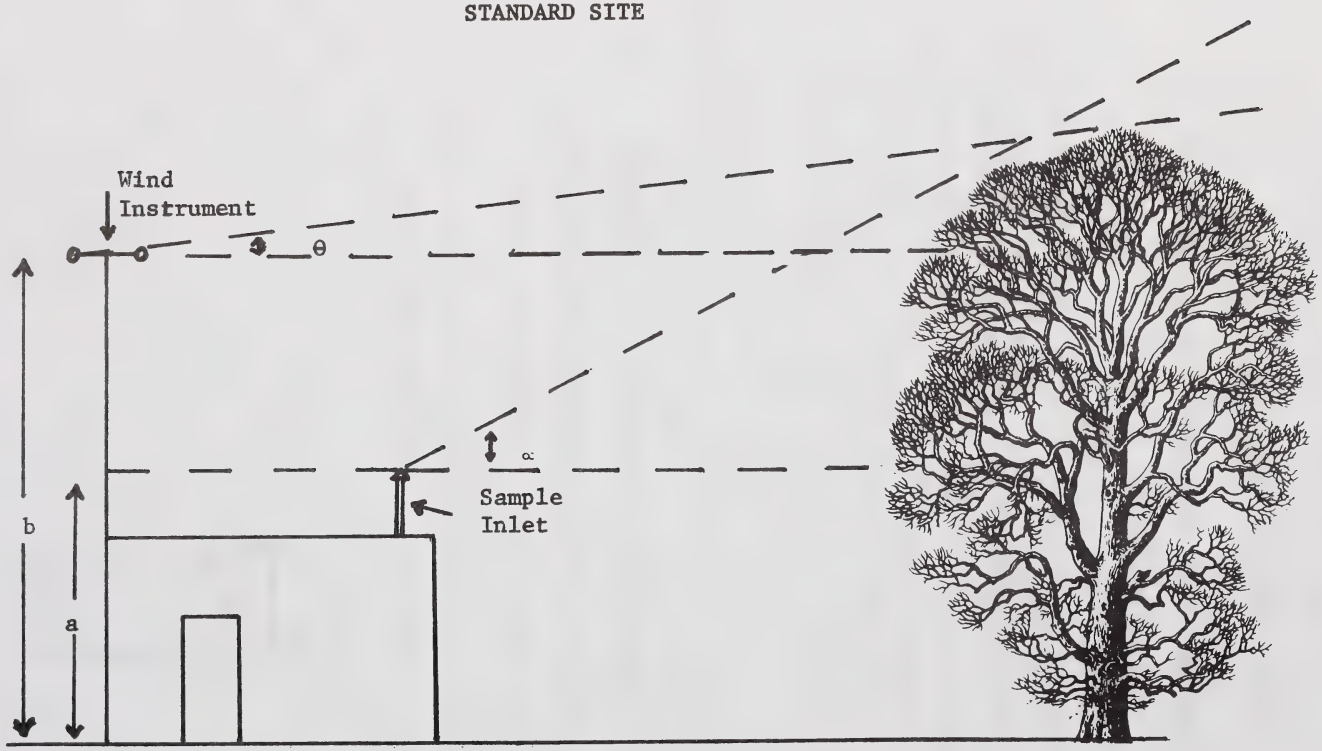


* Anything that significantly alters the air flow in the vicinity of the station.

DIAGRAMMATIC REPRESENTATION

OF A

STANDARD SITE



Where: a = Shelter height + 0.5 m (3m minimum)
b > 2.5 times shelter height (10m minimum)
$\alpha < 30^\circ$
$\theta < 6^\circ$

APPENDIX E

STANDARD MONITORING NETWORK AND SITE DOCUMENTATION

STANDARD NETWORK AND SITE DOCUMENTATION

Complete documentation for an air monitoring network of one or more stations shall include:

1. A recent area map showing roadways, railway lines, airports, lakes, rivers, human settlements, and other significant landmarks; with the station locations clearly indicated.
2. A topographic map showing the station locations (preferred scale is 1:50,000 with elevation contours at 25 foot intervals).
3. The area and topographic maps shall indicate the location of the plant and all petroleum storage tanks and facilities.
4. A wind rose (preferably a ten year average) for the area for existing and new stations (if readily available).
5. A copy of the completed static station documentation table.
6. For each continuous monitoring station:
   a. A copy of the completed site documentation forms.
   b. A current aerial photograph (if it is readily available) covering an approximate area of one square kilometre with the station at the centre of the photograph.
   c. A plan view sketch of the immediate surroundings within a 500 metre radius showing all topographical features, significant vegetation, buildings, and other local disturbances (clearings, pits, towers, etc.) with relevant distances to approximate scale. Heights of obstacles should be noted on the sketch.

d. A cross-sectional sketch through tall obstacles, giving the relevant heights and elevation angles. This sketch is to show obstacles on both sides of the continuous monitoring trailer within a 500 metre radius and also along the line drawn from the plant through the monitoring station.

e. Thirty-five millimetre color print(s) showing the details of the sampling inlet(s) or manifold in relation to the trailer.

f. A 35 mm color print of the structure housing the instruments from the door side, with the direction of the exposure marked on the bottom.

g. Four 35 mm prints showing the station environs looking from the shelter to the East, to the South, to the West, and to the North; with the appropriate direction marked clearly on the bottom.

h. If the station does not conform to the standard site criteria, additional photographs and sketches to illustrate the irregularities.

STATIC STATION DOCUMENTATION TABLE

Static Station Number	Height Above Ground (m)	Significant Features of Surrounding Area

STATION NAME _____ STATION LOCATION _____

INSTRUMENT DETAILS								
Pollutant Measured		Manufacturer	Model No.	Serial No.	Range Used	Detection Principle	Sampling Height in Metres Above	
							Ground	Shelter
Sulphur Dioxide	Analyzer							
	Recorder					N/A	N/A	N/A
Hydrogen Sulphide	Analyzer							
	Recorder					N/A	N/A	N/A
Hydro-carbon	Analyzer							
	Recorder					N/A	N/A	N/A
Wind	Instrument							
	Recorder					N/A	N/A	N/A

APPENDIX F

DETERMINATION OF TOTAL SULPHATION IN AMBIENT AIR BY THE TURBIDIMETRIC METHOD

TOTAL SULPHATION IN AMBIENT AIR

(Turbidimetric)

Introduction

Sulphur gases such as sulphur dioxide, hydrogen sulphide, and mercaptans are common air pollutants. They originate mainly from the burning of sulphur containing fuels such as coal and gasoline, and from the sulphur recovery process of petroleum refineries. These gases are oxidized by lead dioxide to lead sulphate. This oxidation is known under the name of total sulphation. The lead dioxide candle or plate (Huey plate) is commonly used for monitoring sulphur pollution of the atmosphere.

Principle

The lead dioxide candle or plate is exposed in the field for approximately four weeks. The exposed lead dioxide is removed from the support medium and digested with sodium carbonate solution. The unreacted lead dioxide is removed by filtration. The filtrate is acidified to pH 2.5 and the sulphate is precipitated as $BaSO_4$. The resulting turbidity of the $BaSO_4$ suspension is measured in a spectrophotometer at 420 nm.

Scope

The detection limit is 2 mg/l SO_4 in the test solution.

Interference

Colour interferes. Such interference is eliminated by using a sample blank.

Apparatus

1. Jars (20 cm circumference) and Huey plates.
2. Surgical gauze, curity or equivalent (60 cm long, 5 cm wide).
3. Blender.
4. Spectrophotometer.
5. Nessler tube, matched 50 ml, 2.5 cm diameter.
6. Spoon, 0.5 g capacity.

Reagents

1. Lead dioxide (MCB Technical or equivalent).
2. Methanol, 100%.
3. Gum tragacanth (2%) - dissolve 20 g in 100 ml methanol and dilute to one litre with distilled water.
4. Sodium carbonate solution (2%) - dissolve 20 g anhydrous sodium carbonate in distilled water and dilute to one litre.
5. Sodium carbonate solution (1%) - dissolve 100 g anhydrous sodium carbonate in distilled water and dilute to 10 litres.
6. Dilute hydrochloric acid solution (1 + 1) - dissolve 100 ml concentrated hydrochloric acid in 100 ml distilled water.
7. Sulphate reagent - Sulfaver IV (Hach Chemical Company or equivalent).

8. Stock sulphate solution (1000 mg/l SO_4) - dissolve 1.4790 g of anhydrous sodium sulphate in 1% Na_2CO_3 solution and dilute to 1000 ml with 1% Na_2CO_3 solution.
9. Working sulphate standards - dilute each of the following aliquots of 1000 mg/l stock to 900 ml with 1% Na_2CO_3 solution, adjust the pH to 2.5 by adding 1 + 1 HCL with constant stirring. Stir for 10 minutes to drive off the CO_2. Dilute to 1000 ml in a volumetric flask with distilled water:

ml of stock/1000 ml	conc. mg/l SO_4
2.0	2.0
5.0	5.0
10.0	10.0
20.0	20.0
40.0	40.0
50.0	50.0

Procedure

A. Sampling

1. Preparation of the candle - wrap a tape of surgical gauze, 60 cm long and 5 cm wide, around a jar of 20 cm circumference. Secure the gauze to the jar with cotton thread and paint it with a PbO_2 mixture prepared as follows:

   Add 300 ml of 2% gum solution slowly to approximately 300 g of PbO_2, stirring continuously until a smooth paste is obtained. Spread the lead dioxide paste evenly on the

surgical gauze around the jar with a small brush. Each cylinder should contain approximately 8 to 10 g of PbO_2.

2. Preparation of Huey plate - grind 4 g of Gelman paper in a grinding mill and transfer it to a blender containing 400 ml of water. Blend for one minute. Add 64 g of PbO_2 and 22 ml of 2% gum tragacanth solution to the blender and blend for another four minutes. Attach a circular gauze to the plate with acetone by pouring 1 ml acetone into the plate and allowing it to evaporate at room temperature in a fume hood. Pipet 10 ml of the blended suspension into the Huey plate and allow it to dry in an oven at 50 to 55°C.
3. Expose the cylinder and/or two plates in the field for approximately four weeks.

B. Analysis

1. Measure the exposed areas of the painted gauze on the candle and/or the Huey plates in cm^2.
2. Remove the tape from the jar and place it in a 400 ml beaker. Put the two Huey plates and the gauze into a 250 ml beaker. Care must be taken with this step to ensure that no $PbSO_4$ is lost during the transfer. Set up sample blanks by using an unexposed candle and two Huey plates. Use 2% Na_2CO_3 solution for the reagent blank.

3. Add 100 ml 2% sodium carbonate solution to the beaker containing the candle tape, and 50 ml to the beaker containing the Huey plates.
4. Stir the mixtures and allow them to stand for at least three hours.
5. Heat the samples for 45 minutes at approximately 80° C, keeping the volume above 60 ml with distilled water for the candle tape and 30 ml for the Huey plates.
6. Filter the hot samples, rinse the beakers and wash the contents of the filter several times with hot distilled water.
7. Cool the filtrates to room temperature and acidify them with 1 + 1 HCL to a pH of approximately 2.5, stirring constantly. Stir for 10 minutes to drive off the CO_2.
8. Adjust the volume of the filtrate to 200 ml for the candle sample and to 100 ml for the Huey plate sample with distilled water.
9. Pipet 50 ml of sample, sample blank, reagent blank, and working standards into 50 ml Nessler tubes. Add approximately 0.5 g of Sulfaver IV to each tube and stir well. Wait for 10 minutes.
10. Use the reagent blank for setting the spectrophotometer to 100% transmittance at 420 nm,

and read the percent transmittance for all samples, sample blanks, and standards.

Calculation

1. Prepare a calibration curve by plotting mg/l SO_4 vs percent transmittance. Read the concentration for the exposed and unexposed samples from the graph in units of mg/l SO_4. Subtract the value for the unexposed sample from the exposed one to get the actual value. Calculate mg $BaSO_4$ as follows:

$$\text{mg } BaSO_4 = \frac{\text{mg/l } SO_4 \text{ x total sample volume in ml x } 2.43}{1000}$$

$$2.43 = \frac{\text{mol. weight of } BaSO_4}{\text{mol. weight of } SO_4}$$

2. The following equation is used to express the total sulphation in units of mg SO_3/day/100 cm^2:

$$\text{mg/}SO_3\text{/day/100 cm}^2 = \frac{\text{mg } BaSO_4 \text{ x } 0.343 \text{ x } 100}{d \text{ x } a}$$

where d = no. of days exposed

a = surface area of the tape or Huey plate in cm^2

$$0.343 = \frac{\text{mol. weight of } SO_3}{\text{mol. weight of } BaSO_4}$$

100 = converts the result to 100 cm^2

Reference

ASTM, Part 26, 1976, p. 533.

APPENDIX G

DETERMINATION OF HYDROGEN SULPHIDE IN AMBIENT AIR (IODOMETRIC TITRATION)

DETERMINATION OF HYDROGEN SULPHIDE IN AMBIENT AIR (Iodometric Titration)

Introduction

Hydrogen sulphide is a toxic and malodorous air pollutant. It has adverse effects on lead-based paints and is corrosive to certain metals. It originates from pulp and paper plants, and oil and gas refineries.

Principle

Five centimetre wide tape of filter paper, impregnated with a 5% solution of zinc acetate, is exposed to the atmosphere for approximately four weeks. Hydrogen sulphide present in the ambient air reacts with zinc acetate and forms zinc sulphide. The sample is analyzed by decomposing zinc sulphide to hydrogen sulphide with hydrochloric acid, and determined by iodometric titration.

Scope

The method is applicable only to ambient air on a cumulative basis. The detection limit in the test solution is 1 mg/l S°.

Interference

Sulphur dioxide and mercaptans interfere.

Apparatus

1. Jars (20 cm circumference).

2. Filter paper tape (Whatman No. 2, 60 x 5 cm or equivalent).

Reagents

1. Zinc acetate/glycerine solution - dissolve 5 g zinc acetate and 5 ml glycerine in 100 ml distilled water.
2. Stock iodine solution (0.100N) - dissolve 40 g KI in 800 ml distilled water in a 1000 ml volumetric flask, add 12.8 g of iodine and dilute to volume.
3. Standard iodine solution (0.025N) - dilute 125 ml of stock solution to 500 ml in a 500 ml volumetric flask with distilled water. Standardize this iodine solution against a standard thiosulphate solution.
4. Sodium thiosulphate solution (0.025N) - dissolve 12.41 g of sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 2000 ml with distilled water. Standardize against standard potassium dichromate.
5. Potassium dichromate (0.100N) - dissolve exactly 4.904 g of potassium dichromate (dried for two hours at 103° C) in distilled water in a 1000 ml volumetric flask and dilute to volume.
6. Starch solution - prepare a paste by adding 10 g of starch to 20 ml of distilled water. Add two litres of boiling water to the paste and stir until all the starch dissolves. Add a small amount of salicylic acid to prevent mold formation.

7. Standardization of sodium thiosulphate - pipette 10.0 ml of 0.100N potassium dichromate solution into a 400 ml beaker containing 25 ml of water, 2 g KI, and 5 ml of 1 + 5 HCl. Allow the reaction to proceed in the dark for five minutes; dilute to approximately 200 ml and titrate with 0.025N $Na_2S_2O_3$ adding 0.5 ml of starch near the endpoint. At the endpoint the colour changes from opaque blue to a transparent pale green.

$$\text{Normality of } Na_2S_2O_3 = \frac{\text{ml of dichromate x normality of dichromate}}{\text{ml of } Na_2S_2O_3}$$

8. Standardize the 0.025N iodine solution against the above standard $Na_2S_2O_3$ using starch as the indicator.

Procedure

A. Sampling

Preparation of hydrogen sulphide candle - impregnate 60 x 5 cm filter paper tapes with zinc acetate/glycerine solution by soaking them for 15 to 20 hours in the acetate solution. Remove the tapes and allow them to dry until they are just slightly damp. Wrap each tape around a jar and tie it with a string. Expose the candle in the field for approximately four weeks.

B. Analysis

1. Measure the exposed surface area of the tape before removing it from the jar.

2. Remove the tape from the jar.
3. Fold the tape to fit in the bottom of a 600 ml beaker.
4. Add 150 ml of distilled water, thoroughly immersing the tape. Allow it to stand for one hour at room temperature.
5. Add 10 ml of 0.025N iodine followed by 5 ml of concentrated HCL. If, after stirring, the brown colour of the solution disappears, immediately add more iodine in 10 ml portions until the brown colour persists. Record the total amount of iodine added.
6. Titrate with 0.025N sodium thiosulphate adding 0.5 ml of starch towards the endpoint. The endpoint is reached when the blue colour disappears. Read and record titrations to the nearest 0.10 ml.
7. An iodine blank should be run initially and after every tenth sample.

Calculation

1. mg S^{o} = ml of iodine used for the reaction x

$$0.4 \times \frac{0.025}{N} = (C-D) \times 0.4 \times \frac{0.025}{N}$$

where:

C = ml of $Na_2S_2O_3$ used for blank

D = ml of $Na_2S_2O_3$ used for sample

0.4 = mg of sulphide, equivalent to 1 ml of 0.025N iodine solution

N = Normality of $Na_2S_2O_3$ solution.

2. Convert all volumes of iodine to equivalent volumes of sodium thiosulphate. The concentrations of sulphide is expressed in:

units of mg SO_3/day/100 cm^2 = $\frac{ml \times N \times 40 \times 100}{a \times d}$

where:

ml = no. of ml of iodine that reacted with the sulphide in the sample, expressed in terms of ml of standard $Na_2S_2O_3$

N = normality of $Na_2S_2O_3$

40 = equivalent wt of SO_3

a = area of the exposed tape in cm^2

d = no. of days the tape was exposed

100 = converts the result to per 100 cm^2

References

1. Sanderson, H. P., et al. Journal of Air Pollution Control Association, 16 (1966), 328.

2. Wohlers, H.C., and M. Feldstein. Journal of Air Pollution Control Association, 16 (1966), 19.

APPENDIX H

SOIL pH ANALYSIS

SOIL pH ANALYSIS

Introduction

Soil pH can be determined by several chemical analyses. However, the analysis outlined in procedure 3:13 of the "Manaul on Soil Sampling and Methods of Analysis" edited by J. A. Mckeague is to be followed.

Principle

A sample of soil is added to distilled water. The mixture is stirred, and the resulting suspension is allowed to settle. The pH is then measured by the glass electrode in combination with a saturated calomel electrode which provides the reference potential. The glass electrode system is based on the fact that a change of 1 pH unit produces an electrical change of 59.1 mv at 25° C.

Interference

The glass electrode is relatively immune to interference from colour, turbidity, colloidal matter, free chlorine, oxidants or reductants, as well as from a high saline content, except for a sodium error at high pH. The error caused by high sodium ion concentrations at a pH above 10 may be reduced by using special "low sodium error" electrodes. When employing ordinary glass electrodes, approximate corrections for the sodium error may be made by consulting a chart which the manufacturer can furnish for the particular make and catalog number of the electrode.

Temperature exerts two significant effects on pH measurements; the electrodes vary in potential, and ionization of the sample varies. The first effect can be compensated by an adjustment which is provided on the better commercial instruments. The second effect is inherent in the sample and is taken into consideration by recording both the temperature and the pH of each sample.

Apparatus

Equilibrium, as shown by the absence of drift, should be established between the sample and the electrode system before readings are accepted as final. The analyst should constantly be on the alert for possible erratic results arising from mechanical or electrical failures e.g. weak batteries, cracked glass electrodes, plugged liquid junction, and fouling of the electrodes with oily or precipitated materials.

Buffer Solutions

Electrode systems are calibrated against buffer solutions of known pH value. It is good practice to calibrate the electrodes with a buffer whose pH is close to that of the samples, so as to minimize any error resulting from nonlinear response of the electrode. Since buffer solutions may deteriorate because of mold growth or contamination, it may be advisable to prepare the solutions just prior to use by dissolving dry buffer salts in distilled water. Commercially available buffer salts or powders of tested quality may also be used. In making up buffers from

solid salts, it is imperative that all of the material be dissolved; otherwise the pH may be incorrect. Polyethylene bottles are preferable for storage of buffers and samples, although pyrex glassware may be used.

Information on the preparation of three buffer solutions (pH 4, 7, and 9) is given below. Table 1 lists the pH values of the three buffer solutions at various temperatures.

1. Buffer solution, pH 4.01 at 25° C - dissolve 10.21 g anhydrous potassium biphthalate, $KHC_8H_4O_4$, in distilled water and dilute to 1000 ml.
2. Buffer solution pH 6.86 at 25° C - dissolve 3.40 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, and 3.55 g anhydrous disodium hydrogen phosphate, Na_2HPO_4 (both of which have been dried for two hours at 110° to 130° C) in distilled water that has been boiled for 15 minutes and cooled to room temperature. Dilute to 1000 ml.
3. Buffer solution, pH 9.18 at 25° - dissolve 3.81 g sodium borate decahydrate (borax), $Na_2B_4O_7$, in distilled water that has been boiled for 15 minutes and cooled to room temperature. Dilute to 1000 ml.

TABLE 1 -- Effect of Temperature on pH values of Buffer Solutions

Temperature (°C)	pH value of Buffer Solutions		
	pH 4	pH 7	pH 9
0	4.00	6.98	9.46
5	4.00	6.95	9.40
10	4.00	6.92	9.33
15	4.00	6.90	9.28
20	4.00	6.88	9.23
25	4.01	6.86	9.18
30	4.02	6.85	9.14
35	4.02	6.84	9.10
38	4.03	6.84	9.08
40	4.04	6.84	9.07
45	4.05	6.83	9.04
50	4.06	6.83	9.01
55	4.08	6.83	8.99
60	4.09	6.84	8.96

Procedure

1. Dry soil samples for 24 hours at room temperature.
2. Run sample through a #10 mesh sieve prior to weighing.
3. Measure 20 g of soil and place in a small beaker or plastic cup. Add 20 ml of distilled water.
4. Stir several times during the next half hour; let settle for one hour.
5. Measure the pH by immersing the glass electrode into the partly settled suspension (do not immerse it to the bottom of the container) and placing the calomel electrode in the clear supernatant solution. If a combination electrode is used, immerse it in the supernatant solution.

Precision and Accuracy

The precision and accuracy attainable with a pH meter will depend upon the type and the condition of the instrument used, and the technique of standardization and operation. With the proper care, a precision of ±0.02 pH unit and accuracy of ±0.05 pH unit can be achieved with the better battery models. Line-operated instruments, on the other hand, are less accurate--±0.1 pH unit representing the limits of accuracy under normal conditions. A synthetic unknown sample consisting of a Clark and Lubs buffer solution of pH 7.3 was determined electrometrically with a standard deviation of ±0.13 pH unit in 30 laboratories.

Interpretation

Most soils fall into the pH range of 6 to 8. Soil pH values above 8 may indicate the presence of free calcium carbonate ($CaCO_3$), or the presence of excess sodium (Na). Soils above pH 8 are often saline; the degree of salinity can be measured through determination of electrical conductivity.

Soils of pH 6.0 and less may present soil acidity problems to the farmer. At pH 6.0 and less, alfalfa usually does not fix nitrogen efficiently; and at pH values of less than 5.5, other legumes (red clover and alsike) usually do not fix nitrogen as well as at higher pH values. Soils with a pH of less than 5.5 may have quantities of soluble aluminum (Al) and manganese (Mn)

Analyses of soils of less than pH 5.5 for soluble Al and Mn will help in diagnosing the degree of soil acidity damage to be expected.

TABLE 1 -- Effect of Temperature on pH values of Buffer Solutions

Temperature (°C)	pH Value of Buffer Solutions					
	4.00	5.00	6.00	7.00	8.00	9.00
0	4.00	5.09	5.98	7.12	8.06	9.24
5	4.00	5.09	5.98	7.09	8.04	9.18
10	4.00	5.08	5.98	7.06	8.02	9.13
15	4.00	5.08	5.99	7.04	8.01	9.08
20	4.00	5.09	6.00	7.02	8.00	9.04
25	4.00	5.09	6.00	7.00	8.00	9.00
30	4.01	5.10	6.01	7.00	8.00	8.96
35	4.02	5.11	6.02	7.00	8.00	8.93
40	4.03	5.12	6.03	7.00	8.00	8.90
45	4.04	5.13	6.04	7.00	8.00	8.87
50	4.05	5.14	6.05	7.00	8.00	8.85
55	4.06	5.15	6.06	7.00	8.00	8.83
60	4.08	5.16	6.07	7.00	8.00	8.81
65	4.09	5.17	6.08	7.00	8.00	8.79
70	4.10	5.18	6.09	7.00	8.00	8.78
75	4.11	5.19	6.10	7.00	8.00	8.76
80	4.12	5.20	6.11	7.00	8.00	8.75
85	4.13	5.21	6.12	7.00	8.00	8.74
90	4.14	5.22	6.13	7.00	8.00	8.73
95	4.15	5.23	6.14	7.00	8.00	8.72

N.L.C. - B.N.C.
3 3286 06389302 4